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<p>(54) Title: PRINTED CIRCUIT BOARD MANUFACTURE</p> <p>(57) Abstract</p> <p>A process used during manufacture of PCB's comprises protecting metal pads and/or through-holes to provide a tarnish-resistant and solderable coating. In the method the pads and/or through-holes are bright-etched, metal plated, preferably by an immersion process, and treated with a tarnish inhibitor. The tarnish inhibitor may be incorporated into the immersion plating bath. The metal plating is usually with silver or bismuth and the pads and/or through-holes comprise copper.</p>			

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PRINTED CIRCUIT BOARD MANUFACTURE

In the production of a printed circuit board (PCB), in
5 a first (multi-step) stage a "bare board" is prepared and
in a second (multi-step) stage, various components are
mounted on the board. The present invention relates to the
final steps in the manufacture of the bare board, in which
the bare board is coated with a protective layer prior to
10 passing to the second production stage.

There are currently two types of components for
attachment to the bare boards in the second stage: legged
components eg resistors, transistors etc and, more
recently, surface mount devices. Legged components are
15 attached to the board by passing each of the legs through
a hole in the board and subsequently ensuring that the hole
around the leg is filled with solder. Surface mount
devices are attached to the surface of the board by
soldering with a flat contact area or by adhesion using an
20 adhesive.

In the first stage, a board comprising an insulating
layer, a conducting circuit pattern and conductive pads
and/or through-holes is produced. The board may be a
25 multi-layer board having more than one conducting circuit
pattern positioned between insulating layers or may
comprise one insulating layer and one conducting circuit
pattern.

The through-holes may be plated through so that they
are electrically conducting and the pads which form the
30 areas to which the surface-mount components will be
attached in the subsequent component-attachment stage, are
also electrically conducting.

The conductive areas of the circuit pattern, pads and
through-holes may be formed from any conductive material or
35 mixtures of different conductive materials. They are
generally however, formed from copper. Since over time,
copper tends to oxidise to form a copper oxide layer with

poor solderability, prior to passing to the second, component-attachment stage, a protective layer is coated over the pads and/or through-hole areas where it is desired to retain solderability to prevent formation of a poorly 5 solderable surface layer of copper oxide.

Whilst there is more than one way for preparing the bare boards, one of the most widely used processes for making the bare boards is known as the "solder mask over bare copper" (SMOBC) technique. Such a board generally 10 comprises an epoxy-bonded fibreglass layer clad on one or both sides with conductive material. Generally, the board will be a multi-layer board having alternate conductive layers which comprise circuit pattern, and insulating 15 layers. The conductive material is generally metal foil and most usually copper foil. In the SMOBC technique, such a board is obtained and holes are drilled into the board material using a template or automated drilling machine. The holes are then "plated through" using an electroless 20 copper plating process which deposits a copper layer on the entirety of the board: both on the upper foil surfaces and on the through-hole surfaces.

The board material is then coated with a light sensitive film (photo-resist), exposed to light in pre-selected areas and chemically developed to remove the 25 unexposed areas revealing the conductive areas which are the plated through-holes and pads. Generally, in the next step, the thickness of the metal foil in the exposed areas is built up by a further copper electroplating step. A protective layer of an etch resist, which is usually a tin-lead 30 alloy electroplate composition is applied over the exposed and thickened copper areas.

The photo-resist is then removed exposing the copper for removal and the exposed copper surface is etched away using a copper etching composition to leave the copper in 35 the circuit pattern finally required.

In the next step, the tin-lead alloy resist is stripped away.

Since components will not be attached to the copper circuit traces, it is generally only necessary to coat the solder for attaching the components over the through-hole and pad areas but not the traces. Solder mask is therefore 5 applied to the board to protect the areas where the solder coating is not required, for example using a screen printing process or photo-imaging technique followed by development and, optionally curing. The exposed copper at the holes and pads is then cleaned and prepared for solder 10 coating and the protective solder-coating subsequently applied, for example by immersion in a solder bath, followed by hot air levelling (HAL) to form a protective solder coating on the areas of copper not coated with solder mask. The solder does not wet the solder mask so 15 that no coating is formed on top of the solder-mask protected areas.

At this stage, the board comprises at least one insulating layer and at least one conductive layer. The conductive layer or layers comprise a circuit trace. The 20 board also comprises a pad or pads and/or through-hole(s) protected from tarnishing by layer of solder. A single conductive layer may comprise either a circuit trace or pad(s), or both. Any pads will be part of a conductive layer which is an outerlayer of a multi-layer board. The 25 circuit traces on the board are coated with solder mask.

Such a board is ready to proceed to the second stage for attachment of the components. In this second stage, generally attachment of the components is achieved using solder: firstly a layer of solder paste (comprising solder 30 and flux) is applied onto the boards, generally by printing and the components are positioned on the printed boards. The board is then heated in an oven to produce fusion of the solder in the solder paste, which forms a contact between the components and the board. This process is 35 known as reflow soldering. Alternatively a wave soldering process is used in which the board is passed over a bath of

molten solder. In either case additional solder is used over and above any protective solder coating.

The additional complications of attaching both legged components and the surface mount devices and the special requirements for mounting many small closely spaced components have resulted in increased demands on the surface protection coating for the conductive metal to which the components will be attached, on the PCB's. It is essential that the finish applied by the bare board manufacturer does not leave a pad with an uneven surface as this increases the risk of electrical failure. It is also essential that the protective coating does not interfere in the subsequent solder step, thereby preventing formation of a good, conducting bond between the bare board and components. An extra step in which the protective coating is removed would be undesirable.

As explained above, the conductive metal surfaces are generally formed of copper and the protective surface must be applied at the end of the first stage to prevent the formation of non-solderable copper oxide on the copper surfaces prior to the component attachment. This is particularly important because generally speaking, the first stage and the second, component-attachment stage will be carried out on completely different sites. There may therefore be a considerable time delay between formation of conducting pads and/or through holes and the component attachment stage, during which time oxidation may occur. Therefore, a protective coating is required which will retain the solderability of conducting material and enable a soldered joint to be made when the components are attached to the bare boards.

The most common protection coating presently used is tin/lead solder, generally applied using the "HAL" (Hot air levelling) process, an example of which is described in detail above.

HAL processes are limited because it is difficult to apply the solder evenly and the thickness distribution

produced by the use of HAL processes makes it difficult to reliably attach the very small and closely spaced components now being used.

Several replacement treatments for the HAL coating of 5 a solder layer are being introduced. The coatings must enable formation of a reliable electrical contact with the component. They should also be able to stand up to multiple-soldering steps. For example, as described above there are now both legged and surface mount components for 10 attachment to the bare boards and these will generally be attached in at least two soldering operations. Therefore, the protective coatings must also be able to withstand at least two soldering operations, so that the areas to be soldered in a second operation remain protected during the 15 first operation.

Alternatives to the tin/lead alloy solder used in the HAL process which have been proposed include organic protection, immersion tin or tin/lead plating and nickel/gold plating. In the nickel/gold process 20 electroless plating of the copper surfaces is carried out in which a primer layer of nickel is applied onto the copper followed by a layer of gold. This process is inconvenient because there are many process steps and in addition, the use of gold results in an expensive process.

Organic protection for the copper pads during storage 25 and assembly prior to soldering have also been effected using flux lacquer. Its use is generally confined to single-sided boards (ie. boards which have conductive pads on only one side). The coating is generally applied by dip, spray or roller coating. Unfortunately, it is 30 difficult to provide a consistent coating to the board surfaces so limited life expectancy, due to the porosity of the coating and to its inconsistent coating thickness, results. Flux lacquers have also been found to have a 35 relatively short shelf life. A further problem is that in the component-attachment stage, if reflow soldering is to be used to attach the components, the components are held

in place on the underside of the boards with adhesive. In cases where the flux lacquer is thick, the adhesive does not bond the component directly to the printed board, but instead forms a bond between the adhesive and the lacquer 5 coating. The strength of this bond can drop during the fluxing and soldering step causing components to be lost during contact with the solder baths.

One other alternative currently being used is passivation/protection treatment based upon the use of 10 imidazoles or triazoles in which copper-complex compounds are formed on the copper surface. Thus, these coatings chemically bond to the surface and prevent the reaction between copper and oxygen. However this process is disadvantageous because it tends to be inadequate for 15 withstanding successive soldering steps so that the high temperatures reached in a first soldering step tend to destroy the layer which cannot withstand a subsequent soldering operation needed to mount further components. One example of such a process is given in EP-A-0428383, 20 where a process is described for the surface treatment of copper or copper alloys comprising immersing the surface of copper or copper alloy in an aqueous solution containing a benzimidazole compound having an alkyl group of at least 3 carbon atoms at the 2-position, and an organic acid.

25 Processes are also known which provide coatings using compositions which comprise silver.

The three common complexing systems for electroless silver plating processes are either ammonia-based, thiosulphate-based or cyanide-based.

30 The ammonia systems are disadvantageous because the ammonia-containing silver solutions are unstable and explosive azides may tend to form. Thiosulphate systems are disadvantageous for use in the electronics industry because sulphur compounds in the silver coatings formed 35 result in poor solderability so that in the subsequent component-attachment step, a poor electrical contact may be formed between the bare board and the component.

The cyanide-based systems are disadvantageous due to the toxicity of the plating solutions.

In US-A-5318621 an electroless plating solution containing amino acids as rate enhancers for depositing 5 silver or gold onto a nickel coating overlying copper on a circuit board is disclosed. It is described that neither gold nor silver electroless plating baths based on thiosulphate/sulphate will plate directly onto copper because the copper rapidly dissolves without allowing a 10 silver or gold coating to form. In the introduction of this reference, "Metal Finishing Guidebook & Directory" (1993 edition) silver plating solutions comprising silver nitrate, ammonia and a reducing agent such as formaldehyde are mentioned.

15 US-A-4863766 also discloses electroless silver plating, using a cyanide-based plating solution. In Metal Finishing (1983) 81(1), pp 27-30 Russev describe immersion silvering of copper powder from a plating solution containing silver nitrate and a nitrogen complexing agent. 20 In Metal Finishing (1960) August, p 53 Geld describes a silver coating process involving an initial bright dip of the brass or copper substrate, followed by a silver plating step in which a thick coating of silver is plated from a solution of silver nitrate and potassium iodide. The 25 process is for plating of electrical contacts to increase conductivity.

30 In JP-A-04-110474 a base material is plated with silver, dried and subsequently treated with a mercaptan compound to prevent tarnish.

35 In DE-C-4316679 base metals such as copper are coated with palladium in a two-step process including a first-step in which the surface is contacted with a bath containing a palladium salt and an oxidising agent, and in the second step with a bath containing a palladium salt, a complexing agent and formic acid or formic acid derivative. The latter bath may also contain stabilisers for the bath itself, which stabilise the bath against decomposition or

"plating-out". It is suggested that the copper substrate should previously be etched using a non-bright etch bath including persulphate. However such pretreatment steps tend to produce relatively porous coatings. The inventors 5 minimise the porosity of the coating by using the two-step process in the first of which a very thin coating is formed. This reference warns against using silver as corrosion protection due to migration.

The present invention relates to a displacement 10 immersion metal-plating in which a more electropositive metal displaces a less electropositive metal at the surface to be coated. Ions of the more electropositive metal oxidise the substrate metal. A displacement plating process differs from an electroless process because the 15 silver coating forms on the surface of a metal by a simple displacement reaction due to the relative electrode potentials of the oxidisable metal of the surface to be protected and of the silver ions respectively.

It is reported in for example "Modern Electroplating" 20 by F.A. Lowenheim, published by J Wiley & Sons (1963) that silver will plate by displacement on most base metals but that immersion plated silver is poorly adherent. F.A. Lowenheim suggests that when electroplating base metals with silver, it is necessary to deposit first a thin film 25 of silver on the work piece from a high-cyanide strike bath to ensure good adhesion of the subsequent electroplated silver layer.

The present invention aims to provide an alternative 30 to the solder protection coating for the copper or other conducting surfaces of bare boards which require protection from tarnishing between bare board manufacture and the component-attachment stage.

In accordance with the present invention there is provided a method for coating a PCB comprising an 35 insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the process

comprising contacting the pads and/or through holes with a bright-etch composition in a bright-etch step; and subsequently immersion plating the etched pads and/or through holes in a metal-plating step to form solderable
5 plated metal surfaces.

The insulating layer and conducting layer of the PCB will be as described above. They may comprise the insulating layer and conducting circuit pattern of any conventional PCB, respectively. The pads and/or through
10 holes for plating are those areas of the PCB for which solderability must be maintained for attachment of components in the subsequent soldering steps for component-attachment.

The bright-etch step comprises contacting the pads and/or through-holes with a bright etch composition. Such compositions are already known in the industry for other applications and they produce a bright smooth cleaned surface on the conducting metal from which the pads and/or through-holes are formed. In contrast, non-bright etch
15 compositions, such as those which are based on persulphate provide microroughened, cleaned surfaces. The use of the bright etch step allows the formation of a dense, non-porous metal coating, which is particularly suitable for a
20 subsequent soldering step.

Suitable bright-etch compositions are generally aqueous and may be based for example on one or mixtures of more than one of hydrogen peroxide, sulphuric acid, nitric acid, phosphoric acid or hydrochloric acid. The bright etch compositions generally include at least one component
25 which will tend to modify the dissolution of copper in bright-etch compositions.

Particularly preferred bright etch compositions where the metal surface of the pads and/or through-holes comprises copper or a copper alloy are, for example as
30 described in JP 62-188785 A2 (comprising 5.1-10.2 moles/l nitric acid, 4.6-9.2 moles/l sulphuric acid, 0.01 moles/l zinc nitrate and 0.4 moles/l copper nitrate in aqueous

solution); JP 60-190582 (comprising for example 20-50% by weight sulphuric acid (96%), 10-25% by weight nitric acid (67.5%), 0.5-1% by weight hydrochloric acid (35%) and 0.5-1% by weight nonionic surfactant); US-A-3668131
5 (comprising hydrogen peroxide, sulphuric acid and urea additives); Metal Finishing (Feb 1986), 84, (2), 67-70 (comprising sodium dichromate, sulphuric acid, hydrochloric acid, sodium diethyldithio carbonate); Trans Inst. Metal Finishing (Summer 1983), 61, (2), 46-49 (acidified hydrogen peroxide comprising hydrogen peroxide, sulphuric acid and stabiliser); Oberfläche Surf, (Aug 1979) 20, (8), 178-179 (comprising nitric acid and dodecyl pyridinium chloride);
10 US-A-4510018 (comprising sulphuric acid, hydrogen peroxide, fatty acid amine and ammonium compound); US-A-4459216 (comprising 5-100g/l hydrogen peroxide and 100-300 g/l sulphuric acid and aromatic stabiliser); JP 84-038308 (comprising 0.15-0.3 moles/l hydrochloric acid; 0.2-0.4 moles/l phosphoric acid and 0.02-0.1 moles/l sulphuric acid). Where the conducting material of the pads and/or
15 through-holes comprises stainless steel, particularly preferred bright-etch compositions may be as described for example in WO 93-08317; JP 62-238379 A2; DE 1928307; or Tr. Gos. Nauchno-Issled. Proektn. Inst. Osnovn. Khim (1974), 36, 93-97. Where the conducting material is
20 aluminium, a suitable bright-etch is as described in Met. Finishing (July 1986) 84, (7), 55-59.
25

Thus any etch composition which provides a bright, cleaned surface may be used. In the bright-etch step, contact with the bright-etch composition may be by immersion, spray or any other coating technique, such as is described in any of the references above, for sufficient time and at a suitable temperature to enable a bright surface to form on the conducting material of the pads and/or through-holes. Generally the temperature for
30 contact with the bright-etch composition will be ambient and the contact time will be from 5 seconds to 10 minutes,
35

preferably at least 30 seconds, or even at least 2 minutes, and preferably for no greater than 5 minutes.

Generally after the etching step, there will be a post-rinse step comprising rinsing with deionised water and generally without drying, the bare boards then proceed directly to the plating step. Alternatively, an acid rinse step may be included, after the aqueous rinse.

The plating step is an immersion (or displacement) plating step.

In an immersion plating step, the plating composition comprises metal ions of a metal which is more electropositive than the conducting material. The choice of metal ions in the immersion plating solution, therefore depends on the metal to be plated. Since the pads or through-holes generally comprise copper or nickel, suitable examples of plating metals include bismuth, tin, palladium, silver and gold; silver and bismuth ions are particularly preferred.

A particularly preferred immersion silver plating method is described in our copending British application filed today under the reference number 64/2031/00.

As sources of plating metal ions, any water soluble metal salt may be used, for example nitrates, acetates, sulphates, lactates or formates. Preferably silver nitrate is used.

The metal plating ions are generally in the plating composition at a concentration of from 0.06 to 32 g/l (based on metal ions), preferably from 0.1 to 25 g/l, most preferably from 0.5 to 15 g/l.

Contact of the metal surface with the plating solution will generally be at temperatures of from 10 to 90°C, preferably 15 to 75°C, more preferably 20 to 60°C. For example, the temperature of contact with the plating solution will be from 15 to 50°C, most usually from 20 to 40°C.

Contact can be by any method, usually dip, spray or horizontal immersion coating. Spray coating is preferred.

Such contact may be part of a substantially continuous coating process.

The contact time of the plating solution with the metal surface is sufficient to form plated metal surfaces over the metal. Generally the contact time will be from 10 seconds to 10 minutes. A contact time of less than 10 seconds has generally been found to give insufficient coverage with silver coating and although the contact time may be longer than 10 minutes, no additional benefit has been found from a contact time of longer than 10 minutes.

The preferred plating process is an immersion displacement process and not a true electroless plating process. In the preferred plating compositions of the present invention, metal atoms on the surface of the metal are oxidised by the metal plating ions in the solution, so that a layer of plated metal deposits on the pads and/or through holes. The process is self-limiting because when plated metal covers all of the surface sites of metal oxidisable by the plating metal no further reaction and therefore no further deposition occurs.

In a second aspect of the invention there is provided for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising metal plating the etched pads and/or through-holes by contact with a plating composition in a metal plating step to form solderable plated metal surfaces and contacting the plated metal surfaces with a solution of a tarnish inhibitor.

In this aspect of the invention, preferably, prior to contacting the metal surface with the plating composition in the plating step, the metal surface is cleaned. Cleaning may be using an acidic cleaning composition, such as any cleaning composition known in the art. Examples are copper conditioner PC 1144 supplied by Alpha Metals Limited. Where there is a cleaning step using an acidic cleaning solution, generally there will be a rinsing step

prior to contacting the metal surface with the plating solution. Preferably any pre-cleaning will include a bright-etch step.

In both aspects of the invention the tarnish inhibitor 5 may be present in the plating solution itself so that the plating solution comprises the solution comprising tarnish inhibitor. Thus, in a preferred method of the invention, the plated metal surfaces are contacted with a solution comprising a tarnish inhibitor during the plating step 10 (i.e. contact may be during formation of the plated metal surfaces).

Alternatively, the metal surfaces are formed in the plating step and subsequently the formed metal surfaces are contacted with a solution comprising a tarnish inhibitor in 15 a further step. The solution is preferably aqueous, being made up from deionised or otherwise purified water. The composition comprising tarnish inhibitor may additionally comprise solubilisers, for example non-aqueous solvents, surfactants and/or pH buffers.

20 Contact of the composition comprising tarnish inhibitor with the plated metal surfaces will be for at least 5 seconds, preferably for at least 20 seconds. Where the tarnish inhibitor is present in the plating solution, the time of contact is generally determined by the duration 25 of the plating step. Generally, the contact time will be from 1 to 5 minutes. The temperature of contact is most usually from 10 to 90°C, preferably 15 to 75°C, more preferably 20 to 60°C. For example the temperature of contact with the plating solution may be from 15 to 50°C, 30 most usually from 20 to 40°C. Contact may be any conventional means, for example by dip, spray or horizontal immersion coating.

The most appropriate pH depends to some extent on the particular tarnish inhibitor used but primarily on the metal ions present in a plating bath which contains the tarnish inhibitor. Where the tarnish inhibitor is contacted in a separate step with the plated metal surface,

the pH should be appropriate for the tarnish inhibitor and selected so that it does not attack the plating. Where the solution is a silver plating composition a convenient pH is in the range 3 to 10. Where the solution is a bismuth 5 plating bath the pH may be 1 or lower.

The solution comprising the tarnish inhibitor may be a final rinse solution, applied to the boards prior to drying of the boards. The board may undergo subsequent treatment steps after contact with the composition 10 comprising tarnish inhibitor. However, generally, after contact with the solution, comprising a tarnish inhibitor and drying, they are at the end of the first bare board manufacturing stage, and are ready for the second component-attachment stage. Optionally, for example, there 15 may be a deionised water rinse step, prior to drying.

The concentration of tarnish inhibitor in the solution comprising tarnish inhibitor, will generally be from 0.0001 to 5% by weight, i.e. 0.001 to 50g/l. Preferably, the amount of tarnish inhibitor will be from 0.005 to 3% by 20 weight, and most preferably from 0.01 to 2% by weight, or even below 1% by weight.

The method of the second aspect of the invention may surprisingly also be used on precious metals such as gold, platinum or ruthenium where it will improve solderability.

In the second aspect of the invention the metal 25 plating step is preferably an immersion/displacement plating or electroless plating step. It consists of a single step using a single plating composition. Most preferably the plating step will be an 30 immersion/displacement plating step comprising contacting the metal of the pads and/or through-holes with an immersion plating composition.

Where the plating is other than by the preferred 35 immersion/displacement process, for example if it is by electroless plating the plating composition may comprise alternative plating metal ions, such as nickel.

The use of tarnish inhibitor in the invention has been found to provide metal coatings which have good tarnish-resistance (resistance to humidity and oxidation) even when stored at 40°C and 93% RH for 96 hours or at 150°C for 2 hours. The porosity inherent in immersion coatings is reduced by the provision of a level surface using the bright-etch step so that the anti-tarnish properties are considerably improved, even at the high temperatures reached in reflow soldering processes. Concern over the use of silver plating as described for example in DE-C-4316679 due to migration of silver ions is overcome as it has been found that the present invention substantially prevents silver migration by providing a barrier to moisture.

In both the above aspects of the invention, an immersion plating composition preferably contains a complexing agent for the ions of the more electropositive metal.

In a further aspect of the present invention there is provided a displacement metal plating process in which a relatively less electropositive base metal is plated with a relatively more electropositive coating metal by contact with an aqueous plating composition containing ions of the more electropositive metal, a complexing agent for such ions and a tarnish inhibitor for the more electropositive metal so as to form a coating of the more electropositive metal.

In this aspect of the invention there is also provided a new plating composition containing ions of a metal which can be displacement plated, a complexing agent for the ions, preferably present in higher than equimolar amounts as compared to the metal ion, and containing a tarnish inhibitor for the said metal, and being substantially free of reducing agent capable of reducing the ions to the metal.

This aspect of the invention has been found to be particularly useful for silver or bismuth plating.

Therefore preferably, the plating composition described contains silver or bismuth ions.

The plating composition used in this aspect of the invention may be a immersion plating composition based on 5 any plating composition used in the PCB industry.

In this embodiment of the invention, preferably, prior to contacting the metal surface with the plating composition in the plating step, the metal surface is cleaned. Cleaning may be using an acidic cleaning 10 composition, such as any cleaning composition known in the art. Examples are copper conditioner PC 1144 supplied by Alpha Metals Limited.

Where there is a cleaning step using an acidic cleaning solution, generally there will be a rinsing step 15 prior to contacting the metal surface with the plating solution.

Preferably any pre-cleaning will include a bright-etch step.

Where the plating composition comprises a complexing 20 agent it is preferably present in an amount of from 0.1 to 250 g/l, preferably from 2 to 200 g/l and most preferably from 10 to 100 g/l, especially around 50 g/l. The complexing agent may be any complexing agent for the plating metal ions which does not form a water insoluble 25 precipitate under the aqueous and pH conditions of the composition. Mixtures of complexing agents may also be used. It is desirable to use complexing agents which are bi-dentate or higher dentate ligands since the stability constants of such complexes are higher than mono-dentate 30 ligands.

Examples of suitable complexing agents have oxygen-containing ligands, for instance amino acids and their salts, preferably having at least 2 and up to 10 carbon atoms, polycarboxylic acids, usually amino acetic acids, 35 such as nitrilo-triacetic acid or, usually, alkylene polyamine polyacetic acids including ethylene diamine tetracetic acid (EDTA) diethylene triamine pentaacetic

acid, N-hydroxyethyl ethylene diamine triacetic acid, 1,3-diamino-2-propanol-N,N,N,'N,'-tetra-acetic acid, bis(hydroxyphenyl)ethylene diamine diacetic acid, diamino cyclohexane tetraacetic acid or ethylene glycol-bis-[(8-aminoethylether)-N,N'-tetraacetic acid] and N,N,N',N'-tetrakis-(2-hydroxypropyl) ethylene diamine, citrates and/or tartrates, N,N-di-(hydroxyethyl)glycine, gluconates, lactates, citrates, tartrates, crown ethers and/or cryptands.

Particularly preferred complexing agents for silver are EDTA, DTPA and N,N,N',N'-tetrakis-(2-hydroxypropyl)ethylene diamine. The complexing agent should form a soluble complex with plating metal ions in aqueous solution under the pH conditions of the plating solution.

A suitable complexing agent for bismuth is chloride, and it is generally unnecessary to use a multidentate (ie bi- or higher-dentate) ligand complexing agent for bismuth.

The complexing agent is preferably used either in stoichiometric equivalent amounts or in a stoichiometric excess so that all the plating metal ions may be complexed. By stoichiometric we mean equimolar. Preferably the complexing agent is present in a higher molar concentration than the silver ions, the molar ratio preferably being (at least 1.2):1, more preferably (at least 2.0):1, more preferably (at least 3):1.

Suitable tarnish inhibitors for use in all aspects of the present invention include for example:

(a) fatty acid amines, preferably having at least 6 carbon atoms, most preferably at least 10 carbon atoms and generally no greater than 30 carbon atoms, they may be primary, secondary, tertiary, diamines, amine salts, amides, ethoxylated amines, ethoxylated diamines, quaternary ammonium salts, quaternary diammonium salts, ethoxylated quaternary ammonium salts, ethoxylated amides and amine oxides. Examples of the primary, secondary and tertiary amine-type corrosion inhibitors are ARMEEN™ ("denotes trademark). Examples of the subsequent amine-type

corrosion inhibitors are respectively DUOMEEN™, ARMAC™/DUOMAC, ARMID™, ETHOMEEN™, ETHODUOMEEN™, ARQUAD™, DUOQUAD™, ETHOQUAD™, ETHOMID™, AROMOX™, all supplied by Akzo Chemie.

- 5 (b) Purines and substituted purines.
 (c) N-acyl derivatives of sarcosine, such as the SARKOSYL range of products supplied by Ciba-Geigy.
 (d) Organic polycarboxylic acids such as Reocor 190 supplied by Ciba-Geigy.
- 10 (e) substituted imidazoline in which substituents are for example hydroxyl C₁₋₄ alkyl amino or carbonyl-containing groups. Examples include AMINE 0, produced by Ciba-Geigy, especially in combination with a N-acyl sarcosine of category (c)
- 15 (f) alkyl or alkyl benzyl imidazoles, eg undecyl imidazole in which the alkyl group has up to 22 carbon atoms, preferably no greater than 11 carbon atoms and in which the alkyl or benzyl groups are optionally substituted.
- 20 (g) benzimidazoles, especially alkylaryl benzimidazoles in which the alkyl group has up to 22 carbon atoms, preferably no greater than 10 carbon atoms and in which the alkyl or benzyl groups are optionally substituted, for example 2-(p-chlorobenzyl) benzimidazole which is particularly preferred.
- 25 (h) Phosphate esters such as EMCOL PS-413, supplied by Witco.
 (i) Optionally substituted triazole derivatives such as REOMET 42, supplied by Ciba-Geigy. Examples are benzo triazole, tolyl triazole and alkyl substituted triazole derivatives having a carbon number on the alkyl group of from 1 to 22, preferably from 1 to 10.
- 30 (j) substituted tetrazoles, such as 5(3(trifluoromethyl phenyl)) tetrazole, is also a preferred example.

The choice of tarnish inhibitor will depend to some extent upon the metal of the plated metal surfaces, but

this will be clear to a person skilled in the art. For example, if the tarnish inhibitor is to be incorporated into a gold plating bath, the tarnish inhibitor may be a chloride salt, however, in contrast, using a silver plating 5 bath, chloride salts may not be used as they will result in formation of an insoluble silver chloride precipitate.

The tarnish inhibitor is preferably water soluble so that the solution is an aqueous solution. However, water immiscible tarnish inhibitors may be used although it may 10 be necessary to include a surfactant/cosolvent in the solution.

This invention has been found to provide considerable advantages in preventing tarnishing and conferring humidity resistance on the bare boards produced so that additional 15 protection is provided between the bare board manufacture stage and the component-attachment stage. Solderability is found to be enhanced.

A suitable pH for a silver plating composition may be from 2 to 12, but is preferably from 4 to 10. Thus, the 20 composition may be acidic, up to pH 7. Alternatively, the composition may be alkaline, and have a pH of greater than 7, or even greater than 7.5. A bismuth plating solution usually has a low pH of 1 or less.

A buffering agent may be included in the plating 25 composition to ensure that the pH of the composition is within the desired range. As the buffering agent, any compatible acid or base may be included. A compatible acid or base is an acid or base which in the amounts required in the composition does not result in the precipitation out of 30 solution of the silver ions and/or complexing agent. For example hydrogen chloride is unsuitable for a silver plating composition as it forms an insoluble silver chloride precipitate. Suitable examples include sodium or potassium hydroxide or a carbonate salt, or where acids are 35 required, suitable acids may include citric acid, nitric acid or acetic acid. Borates phthalates, acetates, phosphonates may be used but the buffer should not result

in precipitation of the metal salts and preferably does not inhibit the plating rate. An appropriate buffer will be dependent on the desired working pH.

The plating composition may include optional ingredients such as surfactants or wetting agents to improve the coating uniformity. Where surfactants are included, preferably they are introduced into the composition in an amount such that in the plating bath, they will be present at a concentration of from 0.02 to 100 g/l. Preferably they will be incorporated at a concentration of from 0.1 to 25 g/l and most preferably at a concentration of from 1 to 15 g/l. Any standard surfactant or wetting agent useful in a plating bath may be used. Nonionic surfactants are preferred. Particularly preferred surfactants are alkyl phenol ethoxylates, alcohol ethoxylates and phenol ethoxylates such as *Synperonic NP9 (ex ICI), *Synperonic A14 (ex ICI) and *Ethylan HB4 (ex Harcros), respectively (*denotes trade name).

A further optional ingredient which can be included in the plating baths of the present invention are grain refiners. Grain refiners improve the appearance of the plated metal surfaces by causing formation of smaller crystals of plated metal having a more densely packed structure. Suitable examples of grain refiners include lower alcohols such as those having from 1 to 6 carbon atoms, for example isopropanol and polyethylene glycols, for example PEG 1450 (Carbowax Union Carbide). Grain refiners may be incorporated in the composition in amounts from 0.02 to 200 g/l. More preferably, if a grain refiner is included, it will be at concentrations of from 0.05 to 100 g/l and most preferably from 0.1 to 10 g/l. Any non-aqueous solvent should be present in amounts below 50% by weight of the composition, preferably below 30% by weight or even below 10% or 5% by weight of the plating composition.

Other non-active, non-interfering components may be included such as defoamers especially for spray applications (eg, A100 supplied by Dow), dyes etc.

The balance in the composition is water. Deionised 5 water or other purified water which has had interfering ions removed, is used in the plating composition used in the process of the invention.

In order to form the plating composition for use in the processes of the present invention, preferably a 10 solution is firstly prepared comprising deionised water, complexing agent as defined above, and any buffering agent, optionally with the other optional ingredients, and a salt of the more electropositive metal is added as an aqueous solution to the other components which have been formed 15 into a pre-mix. It has been found that this is the most advantageous way to prepare the solution because trying to dissolve the metal salt directly into the plating composition is relatively time consuming and, where the metal is silver, tends to be more vulnerable to photo-reaction which results in precipitation of silver ions out 20 of solution, as a dark precipitate.

Preferably the pH of the composition to which a silver salt is added will be from pH 3 to 10, most preferably from 4 to 8.

25 The components are mixed until they have substantially dissolved. The use of heat for silver dissolution is disadvantageous because again, it may tend to cause the formation of a dark silver precipitate.

After contact of the bare board with the solution 30 comprising tarnish inhibitor, the board is dried. Preferably, there will be no post-rinse step between contact of the board with the solution and drying.

Drying may be by any means, but is generally using 35 warm air, for example treated metal may be passed through a drying oven.

The coating obtained using the method of the present invention produces a surface which is considerably more

uniform and even than that obtained in the conventional HAL processes and, compared with organic protection, the coating is more resistant to soldering operations. Furthermore, the process of this invention is less 5 expensive and simpler than use of the nickel/gold process.

In the subsequent component-attachment stage, the components are soldered onto the plated pads and/or through-holes of the bareboard. The metal of the pad(s) and/or through-holes (generally copper) and plating metal, 10 usually silver, and/or the plating metal and solder may tend to intermix. The bond formed with the components has good electrical conductivity and good bond strength.

After component attachment, finished boards having components attached over the plated layer of the present 15 invention, do not suffer joint reliability problems as do those boards formed using a nickel/gold step.

Example 1

A composition was prepared in which 50g EDTA and 20.4g 20 of solid sodium hydroxide were mixed with sufficient water to dissolve them. A solution comprising 1g silver nitrate in deionised water was subsequently added to the premixture comprising EDTA and sodium hydroxide solution and deionised water was added to 1 litre. Copper double sided circuit boards, having a variety of surface mount feature and 25 plated through holes of various diameter were coated with the silver solution using the following procedure.

Boards were chemically brightened in an aqueous solution of 20% v/v H_2O_2 (35%), 0.5% v/v H_2SO_4 (96%), 2.5% 30 1,4-butanediol for 1 minute. A tap water rinse was then employed, followed by an acid rinse in 10% H_2SO_4 for 1 minute. The boards were given a further water rinse, then immersed in the silver plating solution at 40°C for 4 minutes. After removal from the bath, the boards were rinsed with water and warm air dried. Copper areas of the 35 board were coated with a bright, even silver deposit.

Coated boards were subjected to three passes through a typical IR silver paste reflow profile - see figure 1,

then wave soldered using NR300, an Alpha Metals VOC free, no clean flux. 100% filling of the plated-through holes with solder was achieved.

Further boards were stored in a humidity cabinet at 5 40°C/93% RH for 24 hours before being passed through 3 IR reflow profiles. These boards showed a slight degree of tarnishing on the silver coating. However 100% hole filling was still achieved during subsequent wave soldering with NR 300 flux.

10 Example 2

A silver plating solution was prepared by forming a solution comprising 50g EDTA, 20.4g NaOH, 14g Ethylan HB4 (Akros Chemicals), 3g Crodamet 02 (Croda Chemicals) in 800mls deionised water. To this solution was added a 15 solution of 1g AgNO₃ in 100 mls deionised water. The pH was adjusted to 6.8 by addition of dilute NaOH/HNO₃, then made up to 1 litre with deionised water.

Double sided bare copper boards were coated with the above solution using the procedure as described in example 20 1. 100% filling of plated through holes with solder was achieved during wave soldering with NR300 flux after passage through 3 IR reflow profiles.

Boards stored at 40°C/93%RH for 24 hours prior to 25 passage through 3 IR reflow profiles showed no evidence of tarnishing and soldered well during wave soldering trials, giving 100% hole filling.

Example 3

Double sided bare copper boards were coated using the bath composition and procedure as described in example 1. 30 Following removal of the boards from the silver plating solution and rinsing, the boards were immersed in a solution of 4g Reomet 42 (Ciba-Geigy) in 1 litre deionised water (pH 7) for 1 minute at room temperature. The boards were then rinsed in tap water and warm air dried. A bright 35 even silver coating was produced.

The coated boards were stored at 40°C/93% RH for 24 hours then passed through 3 IR paste reflow profiles. The

boards showed no evidence of tarnishing, and soldered well when wave soldered using NR 300 flux.

Example 4

Coupons of copper strip (5cm x 1cm) were coated with
5 the silver coating as described in example 2. In addition,
further samples were coated with immersion tin, 63/37 Sn/Pb
and two competitors solderability preservative coatings
based on substituted benzimidazole chemistry. The
following coating procedures were applied for the various
10 samples:-

Immersion Tin Coating

Coupons were etched in an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_8$ (5%), H_2SO_4 (5%) for 2 minutes, rinsed with tap water, then
15 rinsed with 10% H_2SO_4 for 1 minute and then rinsed with
deionised water. The coupons were then immersed in an
immersion tin plating solution comprising 33g/l Sn (BF_4)₂,
150 g/l thiourea, 20 g/l fluoroboric acid and 5 g/l
Synperonic NP9 (ex ICI) in deionised water, for 1 minute at
room temperature. The coupons were then rinsed with
20 deionised water and warm air dried.

Sn/Pb Coating

Coupons were etched in an aqueous solution comprising
 $\text{Na}_2\text{S}_2\text{O}_8$ (5%) and H_2SO_4 (5%), rinsed with tap water then with
10% H_2SO_4 and then with deionised water. The coupons were
25 warm air dried. Alpha NR300 flux was then applied to each
coupon. The coupons were then coated 63/37 Sn/Pb by
immersion in molten solder at 250°C for 3 seconds.

Azole 1 and Azole 2

Coupons were etched and rinsed as for the immersion
30 tin samples. Coupons were then immersed in the solution
containing the azole at 40°C for 90 seconds. After removal
from the azole containing solution, the coupons were rinsed
with deionised water, and warm air dried.

The coupons were subjected to a variety of different
35 pre-treatments.

A. No pre-treatment.

B. Passage through 3 solder paste reflow profiles.

- C. Storage at 40°C/93% RH for 96 hours.
 - D. Storage at 40°C/94% RH for 96 hours, then 3 solder paste reflow profiles.
 - E. Storage at 150°C for 2 hours.
- 5 Samples were then soldered using a meniscograph with NR300 flux.

The meniscograph test method monitors the solderability by measuring the net force acting between specimen and solder. The coatings are assessed by the 10 length of time to reach zero wetting force, and the size of the equilibrium wetting force. To achieve good results in wave soldering a short wetting time and high equilibrium wetting force are preferred.

15 The table below shows the wetting times in seconds and wetting forces after 2 seconds immersion in mN/mm for various copper coated samples.

TABLE 1

	Coating	Pre-Treatment	Wet time/sec	Wetting force at 2 seconds
5	Example 2	A	0.7	0.429
	Example 2	B	0.8	0.444
	Example 2	C	0.7	0.429
10	Example 2	D	0.7	0.441
	Example 2	E	0.8	0.438
	Tin	A	0.9	0.488
15	Tin	B	> 5	-0.028
	Tin	C	> 5	0.008
	Tin	D	> 5	-0.148
20	Azole 1	A	0.8	0.439
	Azole 1	B	0.9	0.412
	Azole 1	C	0.9	0.443
25	Azole 1	D	0.9	0.426
	Azole 1	E	1.0	0.421
	Azole 2	A	0.9	0.449
30	Azole 2	B	1.0	0.417
	Azole 2	C	0.9	0.466
	Azole 2	D	1.1	0.310
35	Azole 2	E	1.2	0.296
	Sn/Pb	A	0.8	0.475
	Sn/Pb	B	0.8	0.501
40	Sn/Pb	C	0.8	0.492
	Sn/Pb	D	0.8	0.474
	Sn/Pb	E	0.8	0.492
50				

As can be seen from above, the silver coatings prepared according to this invention have shorter wetting times and higher wetting forces than the Sn and benzimidazole alternative and retain these properties more readily after humidity and heat treatment.

Example 5

A displacement bismuth plating composition was prepared comprising 3.9g bismuth oxide, 183.1g hydrogen chloride (as 37% solution), 490.5g glycolic acid (70%

solution), 265.4g (50% sodium hydroxide solution), 0.077g potassium iodide, 0.003g Synperonic NP9 (ex ICI) and 4g 2p-chlorobenzyl benzimidazole, were added to deionised water to make 1 litre of product solution. Bare boards having 5 copper pads and copper through holes were chemically brightened as described in example 1, then immersed in the plating baths for 2 minutes at 70°C. A coating of bismuth was formed on the surface of the copper having a thickness of 0.05µm. Subsequent solderability and tarnish resistance 10 tests carried out on the plated bare boards showed good results for solderability and tarnish resistance.

Example 6

Double sided bare copper boards were bright etched in an aqueous solution of 50% v/v HNO₃, 10% H₂SO₄, 10% H₃PO₄, 1% HCl for 1 minute at room temperature. Boards were then rinsed in tap water followed by 10% H₂SO₄ for 1 minute. After a further water rinse, boards were immersed in silver plating bath described in example 2 for 4 minutes. at 15 45°C. Boards were then water rinsed and warm air dried.

20 The coated boards were stored at 40°C/93% RH for 24 hours then passed through 3 IR paste reflow profiles. The boards showed no evidence of tarnishing and soldered well when wave soldered using NR 300 flux.

Example 7

25 A silver plating bath was prepared by forming a solution comprising 64.8g diethylene triamine penta-acetic acid, 23.0g NaOH, 14g surfactant Ethylan HB4 (Akros Chemicals), 2.5g Crodamet 02 an ethoxylated 3° amine compound (Croda Chemicals) in 800mls deionised water. To 30 this solution was added a solution of 1g silver nitrate in 100mls deionised water. The pH of this solution was adjusted to 6.9 by addition of dilute NaOH solution or nitric acid. The volume was then made up to 1 litre using deionised water.

35 Double sided bare copper boards were coated using the above solution using the procedure as described in Example 1. 100% filling of the plated through holes was achieved

during wave-soldering of the coated boards using Alpha Metals NR300 flux after passage through 3 I.R. reflow profiles showed no evidence of tarnishing, and soldered well during wave-soldering trials giving 100% hole-fill.

5 Example 8

An immersion silver plating solution was prepared comprising 98.2g deionised water, 1g of nitric acid, 0.1g of silver nitrate, 0.3g of Chemeen C2 (antitarnish) and 0.4g Mazawet DF (solubiliser). The pH was adjusted to 6
10 using a 50% solution of ethylene diamine. The bath produced an adherent silver deposit on copper coupons which showed good solderability and humidity resistance.

Example 9

A bismuth plating solution was prepared containing
15 bismuth trioxide 2.1% wt., hydrochloric acid (22°Be) 46.73% wt., glycolic acid (70%) 49.5% wt., potassium chloride 0.07 % wt., polyethylene glycol 600 0.1% wt., Chemax Chemeen C2 0.2% wt., distilled water 1.2% wt. and tartaric acid 0.1% wt. A further solution was prepared from which
20 the Chemeen C2 was omitted. Samples of copper clad printed circuit material were plated in each of the solutions. These plated samples were then placed in a humidity chamber for 16 hours at 60°C and 95% relative humidity.

After this exposure the samples were examined, and
25 those prepared in the solution without the Chemeen C2 were heavily tarnished. The samples prepared in the solution containing the tarnish inhibitor had a good appearance with minimal oxidation, and when tested showed good solderability.

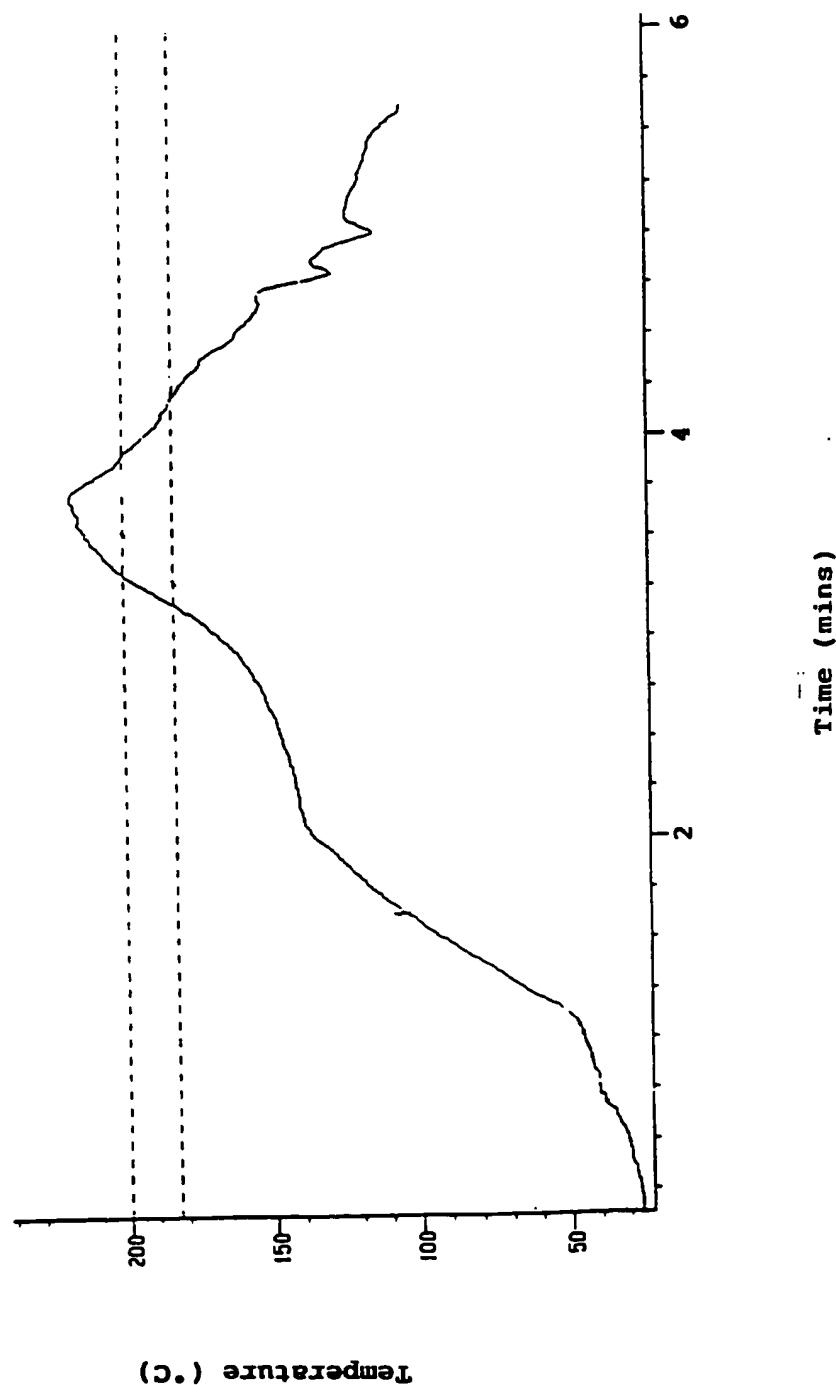
CLAIMS

1. A method for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising contacting the pads and/or through-holes with a bright etch composition in a bright-etch step; and subsequently metal plating the etched pads and/or through-holes by contact with a plating composition comprising ions of a metal which is more electropositive than the metal from which the pads and/or through-holes are formed and being substantially free of reducing agent for said ions in an immersion metal plating step to form solderable plated metal surfaces.
- 15 2. A method according to claim 1 in which the plated metal surfaces are contacted with a solution of a tarnish inhibitor.
3. A method for coating a PCB comprising an insulating layer and a conducting layer, with metal pads and/or through-holes in which the pads and/or through-holes are provided with an anti-tarnish coating, the method comprising metal plating the etched pads and/or through-holes by contact with a plating composition in a metal plating step to form solderable plated metal surfaces and contacting the plated metal surfaces with a solution of tarnish inhibitor.
- 20 4.. A method according to claim 3 in which the metal plating step is a method in which a metal which is more electropositive than the metal of the said pads and/or through-holes is immersion/displacement coated from an aqueous solution containing ions of the more electropositive metal and being substantially free of reducing agent for said ions.
- 25 5. A method according to any preceding claim in which the plating composition contains a complexing agent for the said ions, preferably a multidentate ligand complexing agent.

6. A method according to any of claims 2 to 4 in which the plating composition comprises a tarnish inhibitor and in the process, the metal surfaces are contacted with a solution comprising a tarnish inhibitor during the plating step so that the tarnish inhibitor is present in the metal plating composition.
5
7. A method according to any of claims 2 to 4 in which the metal plated surfaces are formed in the plating step and subsequently the pre-formed plated metal surfaces are contacted with a solution comprising a tarnish inhibitor in a post-rinse second step.
10
8. A method according to any of claims 2 to 4, 6 or 7 in which the contact time of the plated metal surfaces with the solution comprising a tarnish inhibitor is from 10 seconds to 5 minutes.
15
9. A method according to any of claims 2 to 4 and 6 to 8 in which the metal surfaces are contacted with a solution comprising a tarnish inhibitor by dip coating or spray coating.
10. A method according to any of claims 2 to 4 and 6 to 9 in which the tarnish inhibitor is present in the solution in an amount of from 0.001 to 5% by weight of the solution.
20
11. A method according to any preceding claim in which the metal coating of the plated metal surfaces comprise nickel, silver, tin, lead, palladium, cobalt, gold, platinum or bismuth or their alloys, preferably silver.
25
12. A method according to any preceding claim in which the pads or through holes are formed of copper.
13. A method according to any preceding claim including a preliminary step of applying to exposed conductor traces at the surface of the PCB a mask which is an insulator, such that the pads and/or through-holes are left exposed.
30
14. A method according to any preceding claim including a subsequent step of attaching conducting components to the metal plated pads and/or through-holes using solder in direct contact with the metal plating.
35

15. An aqueous plating composition suitable for forming an immersion plating of a relatively more electropositive metal on a relatively less electropositive metal substrate containing ions of the more electropositive metal and a
5 complexing agent for the ions and a tarnish inhibitor for the more electropositive metal and being substantially free of reducing agent for said ions.
16. A composition according to claim 15 in which the tarnish inhibitor is present in the solution in an amount
10 of from 0.001 to 5% by weight of the composition.
17. A composition according to claim 15 or 16 in which the said ions are of nickel, silver, tin, lead, palladium, cobalt, gold, platinum or bismuth or their alloys, preferably silver.

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Figure 1**BEST AVAILABLE COPY**

INTERNATIONAL SEARCH REPORT

Inventor Application No
PCT/GB 95/02877

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C18/42 H05K3/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,43 16 679 (ATOTECH DEUTSCHLAND GMBH) 28 July 1994 see column 3, line 23; example 1 see column 6; claim 10 ----	
A	METAL FINISHING, vol.81, no.1, January 1983, USA pages 27 - 30 RUSSEV 'immersion plating of copper' see page 28, column 2, line 10 - line 20 ----	
A	PATENT ABSTRACTS OF JAPAN vol. 16, no. 358 (C-0970) 4 August 1992 & JP,A,04 110 474 (MEIDENSHA CORP) 10 April 1992 see abstract ---- -/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
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- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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1

Date of the actual completion of the international search

Date of mailing of the international search report

7 February 1996

21.02.96

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INTERNATIONAL SEARCH REPORT

International Application No	PCT/GB 95/02877
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C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	METAL FINISHING, vol.58, no.8, August 1960, USA page 53 GELD 'silver plating of electrical contacts by immersion' -----	

1

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/GB 95/02877

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE-A-4316679	28-07-94	DE-A-	4415211	08-12-94